Isolation of Nano Fibres from Hemp and Flax and Their Thermoplastic Composites

Hemp and Flax Nanofibres and Composites

Suhara Panthapulakkal*[1], Mohini Sain[2]

Centre for Bio-composites and Biomaterials Processing, University of Toronto, Toronto, Cananda M5S 3B3

*[1]s.panthapulakkal@utoronto.ca [2]m.sain@utoronto.ca

Abstract

Agricultural feed stocks are one of the readily available and inexpensive lignocellulosic feed stocks for preparing cellulose nano fibrils. The very common method for isolation and separation of cellulosic fibrils from these feed stocks include successive physicochemical techniques. In this paper, a mild chemical treatment was used to remove pectinic substances and lignin, following a mechanical defibrillation using a commercial grinder to isolate nano fibres from agricultural fibres such as flax and hemp. The defibrillation process was optimized based on the strength properties of the nanofibril films. The generated nano fibres have a diameter distribution in the range of 20-100 nm with 80% fibrils in the range of 20-60 nm. The tensile strength and the modulus of the nano papers were 180-200 MPa and 9-11 GPa compared to 100-95 MPa and 5-6 GPa respectively for hemp and flax. The study showed that, the nano papers can impart high strength even in the presence of hemicelluloses present ed in the fibre bundle indicating removal of hemicelluloses to very low extent using intensive chemical treatments which may not be required for feed stocks with fewer amounts of hemicelluloses, such as agricultural fibres. To exploit the strength properties and reinforcing potential of these nano papers, composites were prepared with polycarbonate. The prepared modulus of the composites showed a significant improvement at a fibre loading of 13 wt%.

Keywords

Bio fibres; Cellulose Nanofibrils; Nanocomposites; Agro- fibres

Introduction

Lignocellulosic materials are well known for their abundance, availability, economic and environmental advantages. These renewable feed stocks, including wood and agricultural biomass such as hemp, flax, jute, ramie and cotton, are the major resources for cellulose fibres. Cellulose is one of the most abundant polymers on the earth and is well known for its industrial use such as in pulp and paper, textile, bio ethanol and so on. Cellulose chains in the plant cell wall are aggregated into a repeated crystalline structure to form the micro fibrils and are interconnected through the loosely arranged cellulose, hemicellulosic and lignin network. This hierarchical structure has to be destructed to generate cellulose microfibrils from this network. Many method have been suggested in the literature to-date including, chemical, mechanical, physico-chemical treatments.

The commonly used physico-chemical methods include acid and alkali treatment to remove pectins and hemicelluloses, and to bleach for removing lignin presented in the plant fibre matrix. Chemical treatments including successive use of sodium hydroxide solution (12-17 wt%) at high temperature, mineral acid (1M), and multiple bleaching were reported to isolate cellulose nanofibres from flax bast fibers, hemp fibers, kraft pulp, rutabaga, and wheat. In another study, cellulose fibrils were isolated from sisal fibres using treatment with sodium hydroxide solution (10 wt% and 17.5 wt%), bleached using hydrogen peroxide or sodium chlorite, and finally acid hydrolysis using sulfuric acid. Li et al. reported an alkali treatment at 130^{o}C and subsequent sulfuric acid hydrolysis to extract cellulose whiskers from the branch-barks of mulberry.

Kaushik et al. extracted cellulose nanofibrils from wheat straw using a combined chemical treatment and steam explosion, followed by high shear mechanical treatment. The method involved two steps: (i) straw fibres were soaked in 2% solution of NaOH overnight and then treated in 10–12% NaOH solution in an autoclave at pressure around 15 lb for 4 h and the fibre were subjected to explosion by sudden release of pressure; (ii) The fibres from first step were then bleached by soaking in 8% solution of hydrogen peroxide (v/v) overnight and then treated with 10% HCl (1N) solution followed by sonication at a temperature around 60^{o}C for 5 h. The washed and

dried fibres then subjected to high shearing to generate nano fibrils. A similar method of steam explosion combined with chemical treatment for extracting cellulose nano fibres from banana fibres were reported by Deepa et al..

Nitric acid-potassium chlorite (HNO3–KClO3) chemical treatment was reported to extract cellulose fibrils from the bamboo samples. For the chemical treatment, 30% nitric acid and 10% wt ratio of $KClO_3$ were employed/utilized and the obtained fibre suspension was then dialyzed, and subjected to acid hydrolysis using sulfuric acid. Chen et al. used consecutive chemical methods to produce cellulose microfibrils from wood, bamboo, wheat and flax. The process involved dewaxing the feedstock using benzene ethanol extraction, lignin removal using multiple stage sodium chlorite bleaching, successive treatment with 2 wt% and 5 wt% potassium hydroxide, at 90°C for 2 h to remove hemicelluloses, residual starch, and pectin followed by washing and ultra sonication.

In all these methods, the lignocellulosics were subjected to strong bases and acids and may have a negative environmental impact. In this study, an attempt is made to extract cellulose nano fibrils from agricultural resources such as hemp and flax bast fibres, using a more environmentally friendly method. The fibres generated by this process were characterized in terms of fibre diameter distribution, crystallinity, and strength properties. Strength of nanofibril films were used for comparison as it is not possible to measure individual fibre strength. Further, to exploit the reinforcing potential of the nano fibre papers, thermoplastic composites were prepared and characterized.

Experimental

Materials

Fibres used for preparation of nano fibres and films were industrial hemp fibres from Hempline Canada (ON, Canada) and spring flax fibres from Saskatchewan, Canada. Polycarbonate film used in this study was from Mcmaster Carr, ON, Canada. All chemicals used in this study were reagent grades.

Preparation of Nano Fibres from Hemp and Flax

The procedure used for the preparation of nano fibres includes a combined chemical and mechanical process where the mild chemical treatments were used to remove pectins and lignin. The cellulose was then defibrillated using a nano fibre facility at the University of Toronto to generate nano fibre suspensions. The detailed procedure of this process is described below.

The treatment protocol involves the stepwise removal of minor and extraneous components such as pectinic substances and lignin from agricultural residue biomass from the agro fibres. The fibres were soaked in water overnight and were disk refined using an 8-inch Sprout-Waldron refiner. The fibre suspension was then treated with 0.05 M hydrochloric acid at 70°C for 2 h. The swollen fibres were cooled at ambient temperature, and neutralized with a solution of ammonium hydroxide to pH 9.5, and soaked overnight to separate the soluble minor and extraneous components such as pectins, starch and fat from the insoluble fibres. The fibres were washed thoroughly with water until the washings were neutral. In the next step, lignin was removed by bleaching using sodium chlorite and acetic acid at a pH of 3-5 for 4 h at 70-75°C (for 100 g fibres dry basis, 13.5 g sodium chlorite and 4.3 mL acetic acid). Sodium chlorite was added in three additions during the 4 h period. The fibres were then washed thoroughly and used for the mechanical defibrillation. The fibres were made into a 2% suspension in water and defibrillated by passing through a commercial grinder (Masuko Corp. Japan). After giving a pre-shear in the grinder without closing the gap between the grinding disks, the fibre suspension was then passed trough the grinder to generate nano fibres. In order to optimize the grinding process, the fibre suspensions were passed 20 times through the grinder and the fibre suspensions after 4, 8, 12, 16 and 20 number of passes were collected for making films.

Preparation of Nano Fibre Films

After defibrillation, appropriate amount of the suspension was diluted with water and vacuum filtered using a membrane filter to produce a thin mat with thickness approximately 50 microns. The films were then dried under pressure for 15 minutes and then dried at 40°C for 48 h and were cut using ASTM die Type E and then dried at 100°C for 2 h to ensure complete drying. The thickness of the samples was measured as an average of 5 points measurements in the tensile specimen.

Chemical Characterization of Nano Fibres and Films

Chemical composition of the original fibres and fibres

after chemical treatment were determined using standard methods. Holocellulose of the fibres determined according to the method described by Zobel and Mc Elwee by dissolving the lignin in an acidic medium with sodium chlorite. Cellulose content was found after extracting hemicellulose from the holocellulose according to the Technical Association of Pulp and Paper Industry (TAPPI) procedure T203 om-93 and the difference between holocellulose and cellulose was reported as hemicellulose content. Lignin content of the fibres was determined according to TAPPI standard T222 om-88. The reported results are the average of three replicates and the variation from the mean was in between 2-5%.

Microscopic Study and Diameter Distribution

Scanning electron microscopy (microscope model Hitachi S-2500) was used to examine the microstructure of hemp and flax fibres before processing in to nano fibres. Prior to SEM examination, the samples were sputter coated with a thin layer of gold to avoid electrostatic charge during examination. Transmission electron microscopy (TEM) was used to study the fibre diameter distribution of generated nano fibres. A drop of dilute nano fibre suspension was deposited on the carbon coated grids and allowed drying before the analysis. Fibre diameter was measured with the help of an image processing analysis program called UTHSCA Image tool down loaded from http://ddsdx.uthsca.edu/dig/itdesc.html. The images from scanning electron microscopy and transmission electron microscopy were loaded into the software package and analyzed. The scale of the software was calibrated using the scale bars on each SEM and TEM images. The diameters of at least 200 fibres from each sample were measured and recorded to get the diameter distribution of the fibres.

X-ray Diffraction Analysis

The crystallinity of the cellulose fibre films before and after defibrillation was examined using a Bruker AXS D8 Discovery Diffraction System (Bruker AXS Inc., Madison, WI, USA) and the procedure was explained elsewhere [8].

Preparation of Nano Fibre – Polycarbonate Composite Film

Nano cellulose-polycarbonate composite films were prepared by pressing the nano fibre sheets from hemp and flax fibres with polycarbonate sheet using compression molding method. The nano sheet was placed in between the polycarbonate sheet and pressed in between the steel plates at a temperature of 210^{o}C under a load of 8000 lb for 1 minute and then under a load of 5 tons for 30 seconds. The composite was cooled at ambient temperature under pressure and left under atmospheric conditions for 24 h before testing. The nano sheets used for making composites were surface treated with isocyanate based polymers and the composites contains about 1.5 wt% of the surface modifier.

Mechanical Properties of the Cellulose Films and Composite Film

ASTM type E tensile specimens were cut from the sheets and tensile properties were measured using a standard computerized testing machine (Instron Model 20) in accordance with the ASTM D-638 procedure with a cross head rate of 2.5 mm/min. All testing mechanical properties were performed at room temperature and the tests for 6 sample specimens for each set was carried out to get the average value.

Results and Discussion

The main purpose for this study was to characterize the nano cellulose fibres prepared by mild chemical treatments followed by mechanical defibrillation and analyse the physical and mechanical properties of nano cellulose sheets and their thermoplastic composite films. The properties of the fibre and their end use mainly depend on the physico-chemical properties of the fibres. Typically any plant fibre consists of cellulose, hemicellulose and lignin as the major constituents along with other minor components such as pectin and waxes.

Chemical composition of the hemp and flax fibres at different stage of chemical treatment are given in TABLE 1. The results indicate that the mild chemical treatment removed the extraneous or pectinic materials from the bast fibres and did not remove the present hemicelluloses. Bleaching using sodium chlorite removes lignin significantly. 85-95% of the lignin and about 94-97% of the extraneous materials were removed from the original hemp and flax bast fibres after the chemical process. Cellulose content of hemp and flax increased from 72% to 84% and from 74% to 84% respectively. The results show that the method used for chemical treatment did not alter the hemicellulose composition in the bast fibres. The pulp fibres used for further mechanical defibrillation has about 99% of holocellulose with 84% of cellulose and

15% of the hemicelluloses.

TABLE 1 CHEMICAL COMPOSITION OF HEMP AND FLAX DURING NANOFIBRE PREPARATION

	Alpha Cellulose	Hemicellulose	Lignin	Other components*
Hemp				
Original	71.7	9.8	9.6	10.9
After HCl/ NH_4OH treatment	80.1	10.4	8.9	0.6
After bleaching	84.2	14.7	0.8	0.3
Flax				
Original	73.6	11.2	7.1	8.1
After HCl/ NH_4OH treatment	81.9	10.5	7.0	0.6
After bleaching	83.9	15.0	0.6	0.5

*Other components calculated as 100-(sum of cellulose, hemicelluloses, and lignin). All the values reported are average of three replicates and the standard deviation varies in between 2-5%

Optimization of the Nanofibril Preparation

The chemically treated hemp and flax fibres were first homogenized by passing through the grinder without closing the gap between the plates of the grinder and then grinded with the highest gap possible for 5 times. These are the initial passes before the actual grinding process and then the pulp fibres were passed through the grinder with minimum gap between the grinders for different number of passes and the fibres were collected after different number of passes. The films prepared out of these suspensions after different numbers of passes were tested for their strength properties after drying at 100°C for 2 h. The results for hemp and flax fibre films are shown in the FIG. 1. Tensile strength and modulus of the pre-sheared papers of hemp and flax are 109 MPa, 86 MPa and 7.3 GPa, and 5.3 GPa respectively.

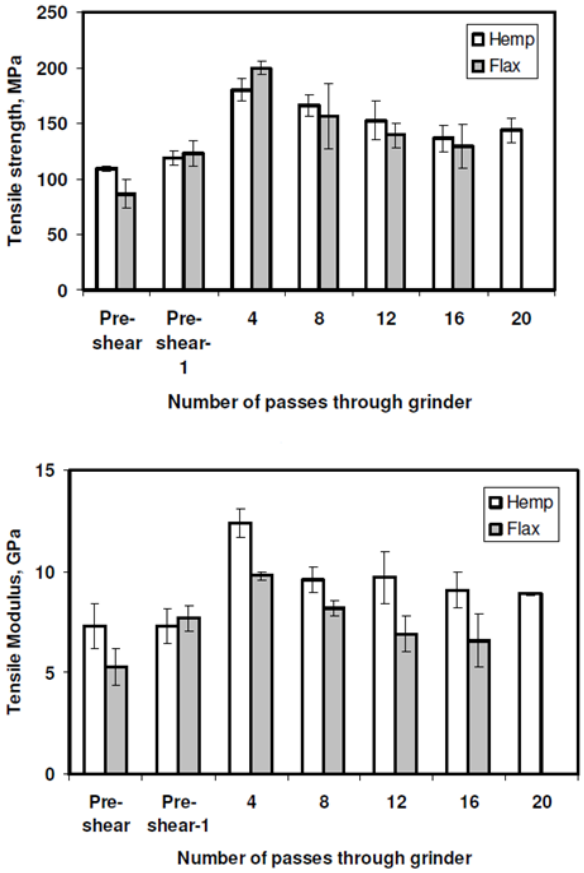

FIG. 1 EFFECT OF GRINDING ON THE TENSILE STRENGTH AND MODULUS OF THE FIBRE FILMS

The strength of the papers increased significantly, to 180 MPa, and to 200 MPa respectively for hemp and flax, upon fibrillation indicating the grinding action open up the fibre bundles to the individual fibres imparting strength to the sheets. The higher strength of papers with defibrillated cellulosic fibres is explained by the high crystallinity of the presented cellulose fibres compared to the original fibres as it is one of the factors contributing to the strength of the cellulosic papers. An enhancement of 65-70% in strength and modulus of hemp fibres upon defibrillation by 4 numbers of passes through the grinder is observed, where as an enhancement of 134% and 84% in the strength and modulus was observed in the case of flax fibres. The difference in strength and modulus of the cellulose fibres is due to the difference in the plant resource as the properties of the cellulose highly depends on the hierarchy of the original cell wall structure.

Role of hemicelluloses on the defibrillation of once-dried wood pulp was studied by Iwamoto et al. who

reported that once-dried pulp with higher amount of hemicelluloses were easily defibrillated in a similar way as that of never dried pulp, compared to the once-dried pulp with lower amount of hemicelluloses. The authors concluded that hemicelluloses can act as inhibitors of the agglomeration of the fibrils during the drying process and facilitate the defibrillation during the grinding process. The results from our study indicates that even the presence of 15% of hemicelluloses in the pulp, can produce nanofibrils that can give high strength to the fibre films. Presence of hemicelluloses might help to the generation of fibrils and prevent the agglomeration of the fibrils as reported by Iwamoto et al.. Hence, it may not be necessary to remove the hemicelluloses completely from the fibres to such a low level as reported in the previous literatures to generate the cellulose nano fibril suspensions. Moreover, by a mild chemical treatment it is possible to avoid harsh chemical environments of the fibre feed stock that may have negative impact on the fibre structure and the environment.

It is clear from the FIG. 1 that the strength and modulus of the papers were decreased slightly after 4 numbers of passes and successively decreased thereafter indicating the damage to the fibrillar structure upon subjecting the fibres for long-time under high shear. Similar results, prolonged grinding decrease the modulus of the strength and modulus of the sheets, reported in the case of wood pulp fibres. However, in both flax and hemp fibres, the strength of the individualized nano fibril sheets was higher than that of the pre sheared fibres. A similar trend was observed in the modulus of the fibre sheets. Since the highest values of strength and modulus of the fibre sheets were observed for the fibres generated after passing through the grinder 4 times, further characterization was carried to compare the pre sheared fibres and the fibrillated sheets after 4 number of passes.

Microscopic Characterization and Fibre Diameter Distribution

Typical scanning electron micrograph and transmission electron micrograph of flax fibres by passing through the grinder after pre-shearing and then after grinding the fibres by passing 4 times are given in the FIG. 2. The mechanical grinding of the fibres resulting in defibrillation of cellulose fibrils from the cell walls as is evidenced from the diameters of the

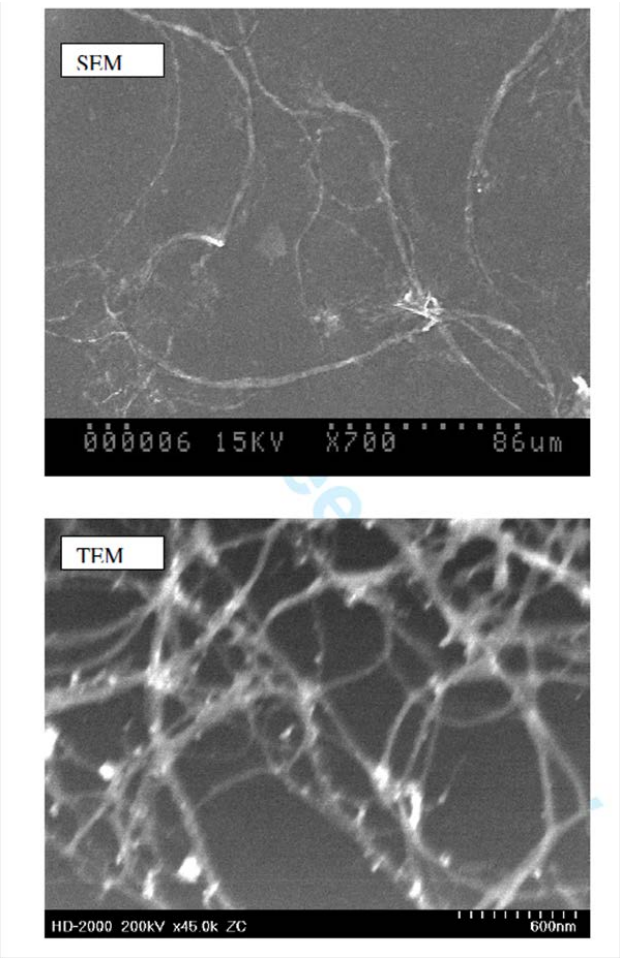

FIG. 2 TYPICAL SEM AND TEM MICROGRPAHS OF FLAX FIBRE BEFORE AND AFTER DEFIBRILLATION

fibres. The average fibre width of the original hemp and flax bast fibres were in 100's of microns and the diameters are considerably decreased after chemical and mechanical defibrillation. The fibre diameter distribution of the hemp and flax fibres after pre-shearing and after defibrillation calculated from the SEM and TEM images using the image processing analysis program, UTHSCSA Image tool, are shown in the FIG. 3. It is clear from the figure that the size of the fibres decreases after preshearing and further defibrillation. After pre-shearing itself, the diameters of the fibres were reduce to 1-5 microns and approximately 70 to 90% of the hemp and flax fibres were in the range of 1-5 microns. The diameters of these pre-sheared fibres further decreased upon shearing by grinding action and the individualized fibrils have a diameter in the range 20-100 nm. Almost 80% of them have a diameter within a range of 20–60 nm and lengths of several thousand nanometres. The diameter distribution of hemp found to be broader compared to flax fibres which have more homogeneous distribution of the fibres is expected to

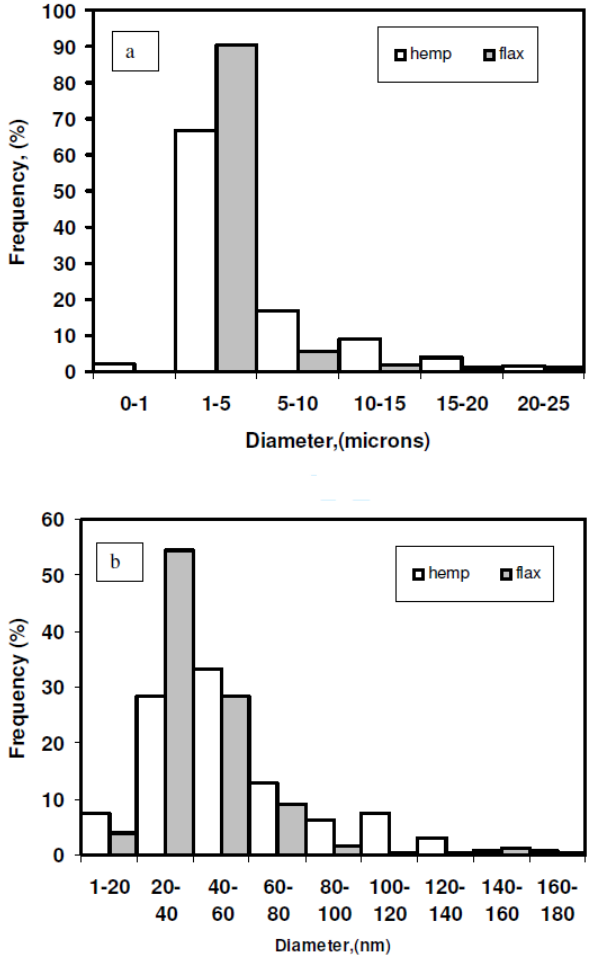

FIG. 3 DIAMETER DISTRIBUTION OF FIBRES (A) BEFORE DEFIBRILLATION (B) AFTER DEFIBRILLATION

TABLE 2 TENSILE STRENGTH AND E-MODULUS OF THE FIBRE FILMS BEFORE AND AFTER DEFIBRILLATION

Property	Hemp Paper	Hemp nano paper	Flax paper	Flax nano paper
Tensile strength, MPa	109 ± 2.3	180 ± 9.6	86 ± 13	200 ± 16
Tensile modulus, GPa	7.3 ± 1.1	12.4 ± 0.7	5.3 ± 0.5	9.8 ± 0.7

have high strength compared to hemp fibres. This observation is in accordance with the strength properties of the films (TABLE 2). The varied fibre distribution might have resulted in the low strength values of the nano fibrillated sheets compared to the more homogenous flax fibrillated sheets.

Crystallinity of the Cellulose Films

Crystallinity of cellulose microfibrils arise from the hydrogen bonds between cellulose molecules and the resulted conformation of the cellulose molecules. It is reported that the length of crystallites in native cellulose can be 100-250nm with cross section of 3-10nm. In plant cell walls, it is believed that the cellulose crystallites are interconnected to each other by disordered cellulose molecules, hemicelluloses and associated lignin network. The crystallinity of the cellulosic fibres highly depends on the source and the degree of degradation of the fibres during chemical and physical method used for the separation of the fibrils from the plant cell wall.

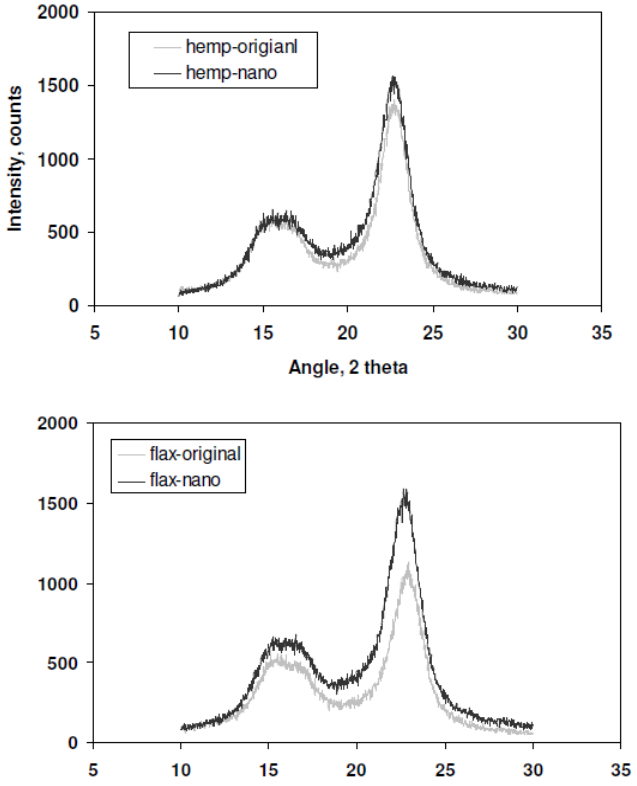

FIG. 4 XRD PATTERNS OF HEMP AND FLAX FIBRES BEFORE AND AFTER DEFIBRILLATION

XRD pattern of hemp and flax films before and after defibrillation is shown in the FIG. 4. Cellulose I is the common variety found in the plants and is characterized by the well defined principal peak at 22.5 (2θ) and the two overlapping secondary peaks at 14.5 and 16.3 (2θ). It was reported that, upon degradation of the cellulose fibre, the two secondary peaks first merged and then destroyed eventually, and simultaneously the principal peak became smaller. It is observed from the FIG. 4 that the expected two secondary peaks merge together and so there is a slight degradation in the cellulosic fibres. Methods for quantifying crystallinity from XRD have been proposed either by using the areas under the peaks or the heights of the maxima and minima of the curve

above the base line. In this paper we used the method of minima and maxima for the calculation of crystallinity index and crystallinity ratio, which is the two ways of expressing crystallinity of cellulose calculated using the following equations

Crystallinity index (C.I.) = I_{max}-I_{min}/ I_{max}

Crystallinity Ratio, (C.R.) = 1 – [I_{min} / (I_{max}-I_{min})],

where I_{max} is the height of the 22.5°(2θ) peak above the base line and I_{min} is the height of the 19° (2θ) minimum above the base line. The crystallinity index and the crystallinity ratios are almost similar and the values for hemp and flax cellulose papers vary from 0.58-0.63 and 0.53-0.62 respectively. The high crystallinity index values show the crystalline nature of the cellulosic papers and are expected to have high strength for these cellulose papers.

Tensile Properties of Cellulose-polycarbonate Composites

From the physical and mechanical properties of the papers, it is clear that papers from defibrillated cellulosic fibres were stronger and it is expected that the composites prepared with these papers would exhibit higher strength and stiffness. Composites were prepared by compressing the nano sheets in between polycarbonate sheets under pressure and temperature.

FIG. 5 shows the results of the comparison of the tensile strength and modulus of the virgin polycarbonate and 12 wt% nano paper reinforced polycarbonate composites. There is a significant increase in the modulus of the composites. Flax cellulose fibril based composite showed higher improvement than the hemp based composite and may be attributed to the better uniformity in the fibre dimensions of flax compared to the hemp fibrils. Modulus of the polycarbonate sheets increases about 1.5 times to 2.5 times by using about 13 wt% of the nano fibrillated sheets. However, it is noticed that there is not much improvement in the strength properties of the composite compared to the virgin polymer. Unlike modulus, breaking strength or ultimate strength of the composite is influenced by the flaws presented in the composite and this could arise from different sources such as poor adhesion between the nano sheet and the polymer, non uniformity in the thickness of the sheets. This will be the subject of future research in the development of thermoplastic nano composites.

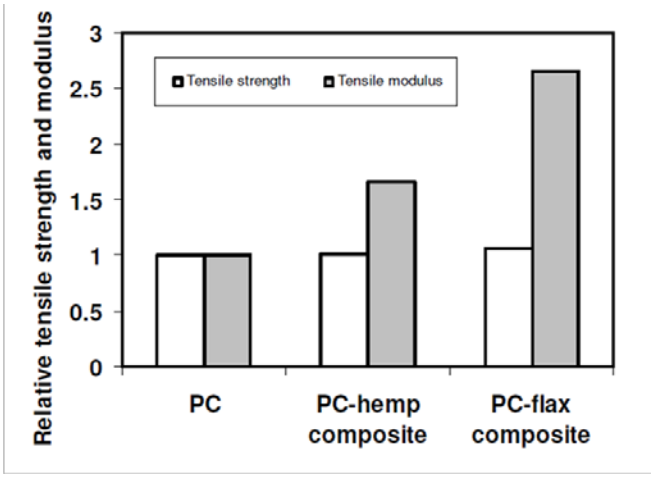

FIG. 5 TENSILE PROPOERTIES OF POLYCARBONATE AND NANOFIBRE-POLYCARBONATE COMPOSITE SHEETS

Conclusions

1. Cellulose nanofibrils were prepared from hemp and flax bast fibres using a chemi-mechanical method, where only lignin and extraneous material were removed in the mild chemical treatment.
2. Nanofibril films were prepared from the suspensions prepared by this process and the results showed that the strength of the papers increased significantly compared to the starting pulps indicating the generation of cellulosic nano fibres from the fibre bundles of the bast fibres.
3. The results also indicated that removal of hemicelluloses from the feed stock is not required to generate microfibrils with high strength performance.
4. Diameters of the produced fibrils were in the range of 20-100 nm and the tensile strength and modulus of the films were found to be around 200 MPa and 10 GPa respectively.
5. The process of grinding for shearing the fibre bundle and to liberate micro fibrils was optimized and found that strength and modulus of the papers were decreasing after 4 numbers of passes through the grinder indicating that 4 numbers of passes were enough to separate nanofibrils from these fibres.
6. Tensile properties of the composites with about 13 wt% of fibres, prepared by compression molding of nanofibril films with polycarbonate sheets showed that there is significant improvement in the modulus of the virgin polymer.

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